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Measurements of hydrocarbon emissions from a boreal fen using the REA technique

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Abstract

Fluxes of biogenic volatile organic compounds (VOC) and methane were measured above a boreal fen. Vegetation on the fen is dominated by *Sphagnum* mosses and sedges. A relaxed eddy accumulation (REA) system with dynamic deadband was designed and constructed for the measurements. Methane, C_2-C_6 hydrocarbons and some halogenated hydrocarbons were analysed from the samples by gas chromatographs equipped with FID and ECD. A significant flux of isoprene and methane was detected during the growing seasons. Isoprene emission was found to follow the common isoprene emission algorithm. Average standard emission potential of isoprene was 680 $\mu g\, m^{-2}\, h^{-1}$. Fluxes of other non-methane hydrocarbons were below detection limit.

1. Introduction

Wetlands cover an area of about 2.5×10^6 km^2, which equals to almost 2% of the total land surface area of the world. Most of the wetlands are located in the boreal and tundra zones on the northern hemisphere (Archibold, 1995). In Finland, the wetlands have covered over one third of the land area but a large portion of the wetlands have been drained for agriculture and forestry during the 20th century. Today there is about 50 000 km^2 of wetland in Finland, which accounts for about one sixth of the total land surface area (Vasander, 1996). Wetland ecosystems are known as a major source of atmospheric methane (e.g. Enhalt et al., 2001) but they have also been reported to emit volatile organic compounds (Klinger et al., 1994; Janson and De Serves, 1998; Janson et al., 1999; Varner et al., 1999; Dimmer et al., 2001; Rinnan et al., 2005).

Volatile organic compounds (VOC) are a diverse group of substances that have many impacts on the atmospheric chemistry. They react with ozone, nitrate and hydroxyl radicals and produce oxygenated compounds such as aldehydes, ketones and organic acids. High VOC concentration together with NO_x can increase ozone levels in the

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lower troposphere (e.g. Chameides et al., 1992) and form organic aerosols (e.g. Kulmala et al., 2000). It is known that monoterpenes ($C_{10}H_{16}$) participate in aerosol formation (Hoffmann et al., 1997) and recently evidence for the aerosol formation ability of isoprene (C_5H_8) has been discovered (Claeys et al., 2004).

Methane, often excluded from VOCs, is an important greenhouse gas. Expressed as a global warming potential within 100 year time horizon methane is about 23 times more efficient greenhouse gas than carbon dioxide (Enhalt et al., 2001). Most important natural sources of methane in the global scale are wetlands and termites. Anthropogenic sources include agriculture, ruminants, energy production, biomass burning and landfills (Enhalt et al., 2001). Wetlands produce methane by anaerobic decomposition of organic matter. Anaerobic layer depth is regulated by water table depth and the microbial production of CH_4 is controlled by soil temperature (e.g. MacDonald et al., 1998).

Significant atmospheric concentrations of biogenic VOCs, e.g. monoterpenes, isoprene and other light hydrocarbons, have been measured in the boreal areas. Scaling the concentrations by the reactivity with ozone and OH-radical shows that biogenic compounds dominate over anthropogenic compounds in rural and remote sites (Laurila and Hakola, 1996; Hakola et al., 2000). Globally the emissions of VOCs are dominated by biogenic sources (Guenther et al., 1995). Also in the boreal regions of Northern Europe the biogenic VOC emission is estimated to exceed the anthropogenic sources (Simpson et al., 1999; Lindfors et al., 2000).

Most of the work aimed at quantifying the VOC emissions from boreal ecosystems has been conducted in forest ecosystems. The VOC emissions from boreal plant species have been measured by e.g. Isidorov et al. (1985), Janson (1993), Hakola et al. (1998, 2001), Janson et al. (1999) and Janson and DeServes (2001) using enclosure techniques. The coniferous tree species in the European boreal zone are observed to emit monoterpenes and carbonyls (Janson, 1993; Janson and DeServes, 2001). However, Norway spruce (*Picea abies*) has been measured to emit also isoprene (Janson and DeServes, 2001). Some of the boreal broadleaved tree species,

such as European aspen (*Populus tremula*) and tea-leafed willow (*Salix phylicifolia*) are found to be high isoprene emitters (Hakola et al., 1998). In addition to the enclosure techniques, VOC emission of boreal forest ecosystems have been measured by micrometeorological flux measurement techniques by Pattey et al. (1999), Rinne et al. (1999, 2000a, 2000b) and Spanke et al. (2001).

Measurements of VOC emissions conducted in boreal wetlands have been reported by Klinger et al. (1994), Janson and De Serves (1998) and Janson et al. (1999). They observed high isoprene emissions. Varner et al. (1999) and Dimmer et al. (2001) reported also emissions of halogenated hydrocarbons, such as methyl chloride, methyl bromide and chloroform, from midlatitude wetlands. Rinnan et al. (2005) identified emissions of various VOC substances from peatland microcosms. All these measurements were performed with chamber technique.

We performed ecosystem level flux measurements of several VOCs, including some halogenated hydrocarbons, using the REA technique, with the aim to quantify the ecosystem level emission rates of these compounds.

2. Materials and methods

The measurements were carried out at Siikaneva fen, located in southern Finland (61°48′ N, 24°09′ E, 160 m a.s.l.), in the southern boreal zone. Siikaneva is about five kilometres west from Hyytiälä Forestry Field Station and SMEAR II measurement station. The annual mean temperature in the area is 3°C. The warmest month is July with mean temperature of 16°C and the coldest is February with mean temperature of −8°C. The annual mean precipitation is 700 mm (Drebs et al., 2002). About one third of the precipitation falls down as snow.

Siikaneva is an open aapa fen. Vegetation is dominated by mosses (*Sphagnum baltucum, S. majus and S. papillosum*), sedges (*Carex rostrata, C. limosa, Eriophorum vaginatum*) and Rannoch-rush (*Scheuchezeria palustris*). Many other species are also present in small amounts. The fen is surrounded by coniferous forests. Homogenous

fetch extends from the measurement site up to about 200 m in south and north and to several hundreds of metres in east and west.

Flux measurements were performed with the relaxed eddy accumulation (REA) technique. The principle of REA method was originally proposed by Businger and Oncley (1990) and ever since it has been widely applied for flux measurements of trace gases and aerosol particles (e.g. Guenther et al., 1996; Pattey et al., 1999; Christensen et al., 2000; Gaman et al., 2001; Lee et al., 2005; Olofsson et al., 2005). In the REA system air samples are accumulated in two separate reservoirs during updrafts and downdrafts. Vertical flux F is given by

$$F = \beta\sigma_w(C_{\mathrm{UP}} - C_{\mathrm{DOWN}}), \quad (1)$$

where β is an empirical dimensionless coefficient, σ_w is the standard deviation of the vertical wind velocity w and C_{UP} and C_{DOWN} are average concentrations of updraft and downdraft reservoirs, respectively. A deadband (sampling threshold), where air parcels with low vertical velocity are not accumulated, is often used.

We designed and constructed a REA system that is suitable for flux measurements of light hydrocarbons. Sonic anemometer (METEK USA-1), with 3-D head correction, measures three dimensional wind speed vector ten times per second. Sonic data is read in real time by a computer which calculates 30 s running box averages of wind speed components as well as other statistics. After each wind measurement a decision of which valve should be open is made. The REA system employs a dynamic deadband with threshold of $\pm 0.5\sigma_w$, where σ_w is the running standard deviation. This increases the concentration difference between the two reservoirs thus decreasing the precision requirement for the chemical analysis. The dynamic deadband also forces the parameter β to become practically constant (β=0.41) and independent of turbulence intensity or atmospheric stability (Christensen et al., 2000; Ammann and Meixner, 2002; Grönholm et al., 2005[1]). For further details of the REA control software used in

[1] Grönholm, T., Rinne, J., Haapanala, S., Rannik, Ü., and Vesala, T.: The dependence of the β coefficient of REA system with dynamic deadband on atmospheric conditions, Environ.

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this study, see Gaman et al. (2004).

Schematic of the REA system is shown in Fig. 1. Air samples were taken in through ozone scrubbers that consist of three plies of MnO_2-coated net. Three plies was found to be a reasonable compromise between ozone destruction efficiency and undisturbed sampling (e.g. Calogirou et al., 1996; Hakola et al., 2003). Air is drawn through PFA tubing with 3 mm inner diameter to valves with ETFE body (Bürkert 117). Air samples are accumulated in Tedlar-bags (SKC 231, 10 l). The sample bags are located inside airtight boxes. Bags are filled by pressure difference between the box and ambient air, thus avoiding potentially contaminating pumps in the sampling system. Pressure difference is achieved by pumping air out from the boxes through a critical orifice ($Q=1\,l\,min^{-1}$). The flux measurement height was 3 m.

After the half hour sampling period the air samples were pumped with a Teflon coated pump from the bags into previously evacuated stainless steel canisters (BRC Rasmussen, 0.85 l) for non-methane hydrocarbon analysis and plastic syringes (50 ml) for methane analysis.

Chemical analysis of the canister samples was done at the Finnish Meteorological Institute for 24 different C_2-C_6 substances and seven halogenated hydrocarbons. The samples were analyzed within one week of the sampling using a gas chromatograph (HP-6890) with an Al_2O_3/KCl PLOT column (50 m×0.32 mm i.d.). Light hydrocarbons and halogenated hydrocarbons were analyzed simultaneously from the same sample. The analytical column was split into two detectors. Flame ionization detector (FID) was used for light hydrocarbons and electron capture detector (ECD) for halogenated hydrocarbons. The samples were pre-concentrated in cold trap using liquid nitrogen before analysis. The light hydrocarbons were calibrated using the VOC mixture standard from the NPL laboratory (UK) and halogenated hydrocarbons were calibrated using standard from NOAA (US). A detailed description of the analysis is given by Hakola et al. (2000).

Methane analysis from the syringes was done at the Hyytiälä Forestry Field sta-

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tion within one day of the sampling. An HP-5890A gas chromatograph equipped with 6 ft×1/8″ column and a FID was used. Four separate analyses were taken from each syringe and the median concentration was used for flux calculation.

Supporting meteorological measurements at Siikaneva includes air temperature at 1.5 m height, air humidity, intensity of photosynthetic photon flux density (PPFD), soil temperatures at depths of 5 cm and 20 cm and water table height. These are stored as ten minutes averages.

To ensure that the assumptions of the micrometeorological method were fulfilled, periods when the average friction velocity had been below 0.1 m s^{-1} were discarded from the data analysis.

The measurements were performed during growing seasons of 2004 and 2005, altogether on 13 separate days. The first period was between 8 July 2004 and 6 October 2004 and the second was between 25 May 2005 and 1 July 2005. Measurements performed on 14 April 2005, before beginning of the growing season, are not included in the data analysis.

3. Results and discussion

In Fig. 2 an example of updraft and downdraft concentrations of selected hydrocarbons together with their uncertainties are shown. Uncertainties were obtained by parallel analysis of light VOC samples taken regularly at Utö and Pallas (Laurila and Hakola, 1996). In Table 1 the mean concentrations of hydrocarbons at Siikaneva, precision of the chemical analysis and flux detection limit are shown. The flux detection limit is derived using the Eq. (1) by substituting the concentration difference with the uncertainty of the analysis and by using typical value of σ_w (σ_w=0.4 m s^{-1}). In April 2005 the isoprene concentrations of both updrafts and downdrafts were nearly zero and thus these measurements were excluded from the further analysis.

In Fig. 3 examples of measured methane and isoprene fluxes during one day are shown. Methane fluxes typically varied between 0 mg m^{-2} h^{-1} and 10 mg m^{-2} h^{-1}.

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Mean methane emission during the whole measurement period was 5.1 mg m^{-2} h^{-1}. This agrees well with the fluxes measured at Siikaneva by enclosure method (Terhi Riutta[2], unpublished data) and eddy covariance method (unpublished data) and those measured over a boreal fen in Saskatchewan by Suyker et al. (1996). Water table height and soil temperature are known to affect methane production and emission from wetlands. However, no clear dependence was observed in this study. This might be due to small data set and rather inaccurate methane flux detection.

The highest observed flux of non-methane hydrocarbons was that of isoprene. Isoprene fluxes varied typically between 0 and 400 μg m^{-2} h^{-1}. These fluxes are in same range with the emissions measured from a boreal fen by Janson and De Serves (1998) and Janson et al. (1999). The daytime isoprene emission rates from Siikaneva were in the same range than the monoterpene emissions from boreal forests (Rinne et al., 1999, 2000a, 2000b; Spanke et al., 2001). The fluxes of other VOCs were below the detection limit of the measurement system.

Isoprene emissions are known to be light and temperature dependent. This dependence can be empirically explained by an algorithm presented by Guenther et al. (1993) and Guenther (1997). According to the algorithm, isoprene emission I is given by

$$I = I_S C_L C_T, \tag{2}$$

where I_S is the standard emission potential at standard temperature (303 K) and standard PPFD (1000 μmol m^{-2} s^{-1}). Light dependence factor C_L is defined by

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}}, \tag{3}$$

where α (=0.0027) and C_{L1} (=1.066) are empirically determined coefficients and L is

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PPFD (in μmol m^{-2} s^{-1}). Temperature dependence factor C_T is defined by

$$C_T = \frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_ST}\right)}{C_{T3} + \exp\left(\frac{C_{T2}(T-T_M)}{RT_ST}\right)}, \quad (4)$$

where C_{T1} (=95 kJ mol^{-1}), C_{T2} (=230 kJ mol^{-1}), C_{T3} (=0.961) and T_M (=314 K) are empirically determined coefficients, R is the universal gas constant (=8.314 J K^{-1} mol^{-1}), T_S (=303 K) is the standard leaf temperature and T is the actual leaf temperature (in K).

We calculated light and temperature dependence factor (C_LC_T) for each measurement using measured PPFD and air temperature. Air temperature was used instead of leaf temperature as the latter was not available. In Fig. 4 the relation between the measured isoprene flux and C_LC_T is shown. Linear fit gives the standard emission potential of 680 μg m^{-2} h^{-1}. This agrees well with the results of Janson and De Serves (1998), who reported average standard emission potential of 708 μg m^{-2} h^{-1} from boreal wetlands.

There seems to be some systematic deviation of the measured fluxes from the emission algorithm. In Fig. 4 it can be seen that the fit seems to be different for low (<0.2) and high (>0.2) values of C_LC_T. The same is true for monthly subsets of the data. Fit to data where C_LC_T is below 0.2 leads to standard emission potential of 330 μg m^{-2} h^{-1} and data where C_LC_T is over 0.2 leads to standard emission potential of 740 μg m^{-2} h^{-1}. One possible explanation is that the emission algorithm does not take into account the differences in the light penetration into the vegetation canopy at different solar angles. The solar radiation might penetrate deeper into the moss at higher solar angles leading to higher isoprene emission rates than obtained by the algorithm. Similarly the relatively inefficient penetration at low solar angles would lead to lower than predicted isoprene emission. This would lead to similar systematic differences between the observed emissions and the emission algorithm. Another source

of systematic error was the use of ambient air temperature instead of leaf temperature. This might also lead to the underestimation of the flux at high solar elevations when the radiation most effectively warms the surfaces. Leaf temperature of mosses and other wetland vegetation is virtually impossible to measure directly.

Seasonal development seems to have only a weak effect to the isoprene flux during the growing seasons. Emission potentials obtained using the data from September, October or May, separately, are lower than the mean emission potential but due to the small datasets it is impossible to say whether this is explained just by low $C_L C_T$ values at these times.

Using the emission potential obtained from the measurements and meteorological data from nearby Hyytiälä station daily emissions of isoprene for the growing season 2004 were calculated (Fig. 5). In the beginning of May 2004 there was an exceptionally warm period. On the other hand, in the end of July there was cold and rainy period. According to the model, total isoprene flux from Siikaneva fen during the growing season 2004 was 150 mg m^{-2}.

4. Conclusions

In the present study, emissions of various light hydrocarbons from a boreal fen were measured using the REA technique. Significant fluxes of methane and isoprene were measured during the growing season. The measured isoprene emissions were observed to follow the isoprene emission algorithm (Guenther, 1997) with standard emission potential of 680 μg m^{-2} h^{-1}. Mean methane emission over the whole measurement period was 5.1 mg m^{-2} h^{-1}, which is in the same range than the fluxes measured by other techniques. Large temporal variations occurred in the methane flux. Fluxes of the other light hydrocarbons and halogenated compounds were below detection limits.

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Table 1. Analyzed non-methane hydrocarbons, their mean concentrations, average standard deviation of parallel samples and corresponding flux detection limit.

Substance	Mean concentration [ppt]	Standard deviation [ppt]	Flux detection limit [$\mu g\,m^{-2}\,h^{-1}$]
ethane	949	53	38
ethene	211	34	22
propane	279	26	27
propene	47	15	15
2-methylpropane	70	9	13
ethyne	205	25	15
butane	97	25	34
trans-2-butene	10	5	7
1-butene	18	8	11
2-methylpropene	51	17	22
cis-2-butene	3	6	8
2-methylbutane	70	7	12
pentane	83	6	10
propyne	8	8	8
1,3-butadiene	2	21	26
trans-2-pentene	7	12	20
cis-2-pentene	7	10	17
cyclohexane	67	2	5
2-methylpentane	26	3	6
3-methylpentane	49	2	5
hexane	146	3	6
isoprene	232	9	14
heptane	38	5	11
benzene	67	11	21
CFC-12	538	14	41
methyl chloride	520	45	53
trichlorofluoromethane	259	7	23
dichloromethane	28	8	16
tetrachloromethane	55	21	77
tetrachloroethene	5	1	5

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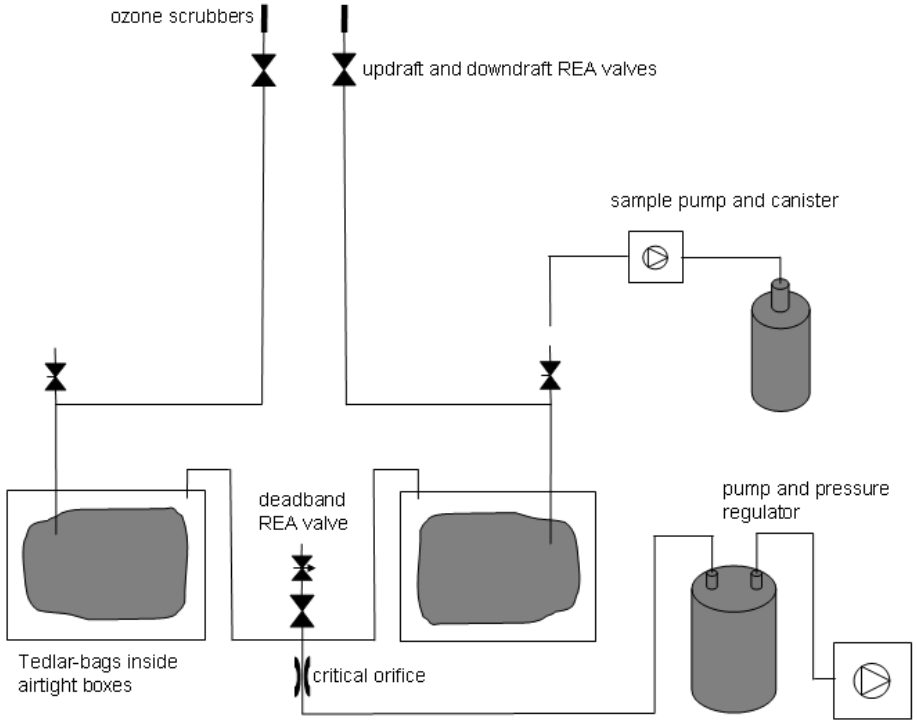

Fig. 1. A block diagram of the REA flow system used in this study.

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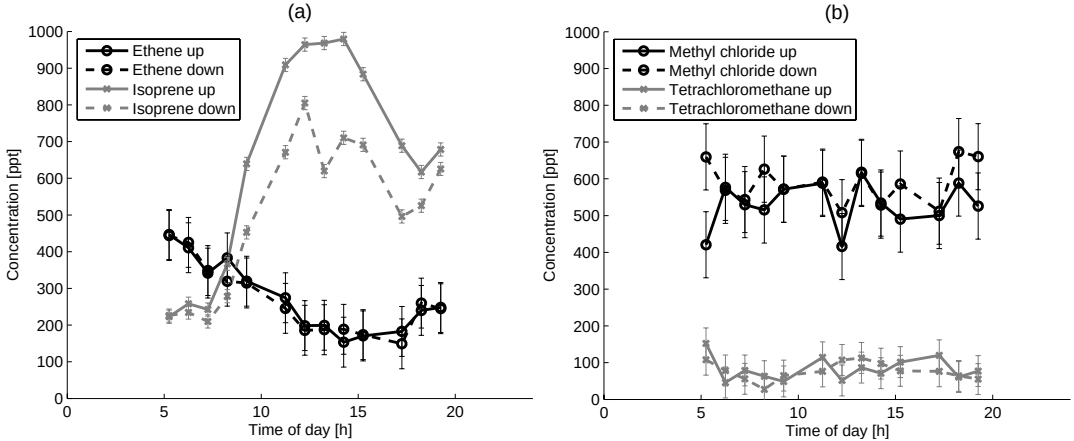

Fig. 2. An example of updraft and downdraft concentrations on 4 August 2004 of selected **(a)** light hydrocarbons and **(b)** halogenated hydrocarbons together with their uncertainties.

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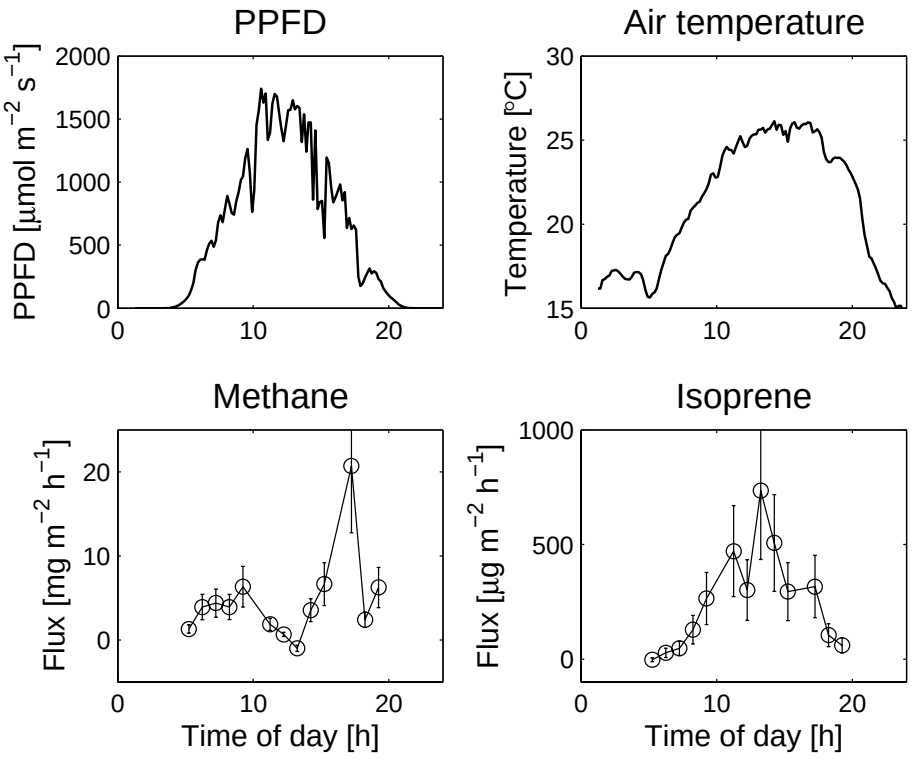

Fig. 3. Measurements on 4 August 2004. Upper panels show PPFD (photosynthetic photon flux density) and air temperature. Lower panels show measured fluxes of methane and isoprene and their error estimates.

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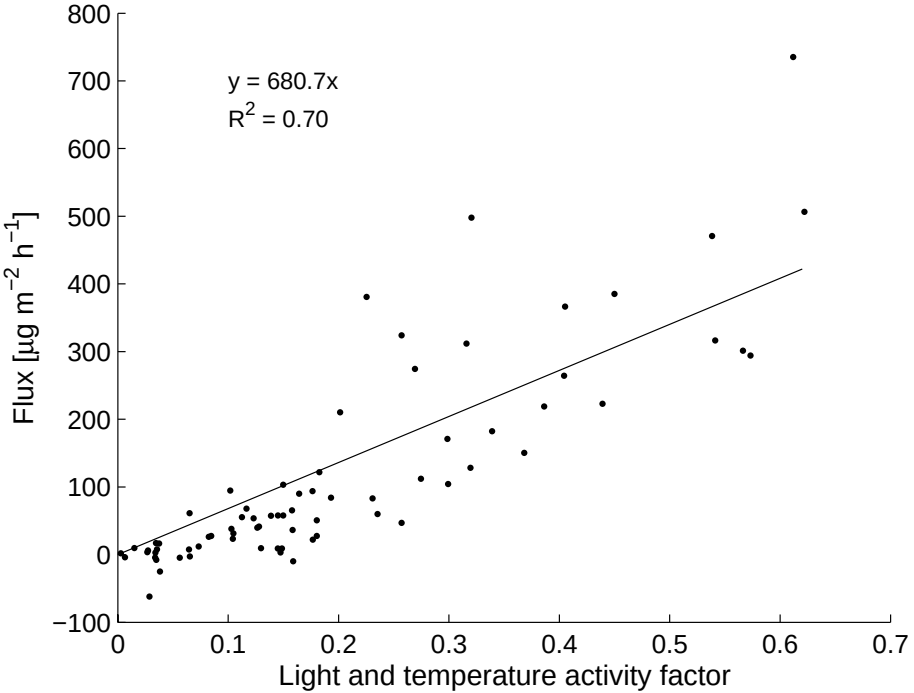

Fig. 4. Measured isoprene flux versus light and temperature activity factor ($C_L C_T$). Linear fit of the dataset determines the standard emission potential.

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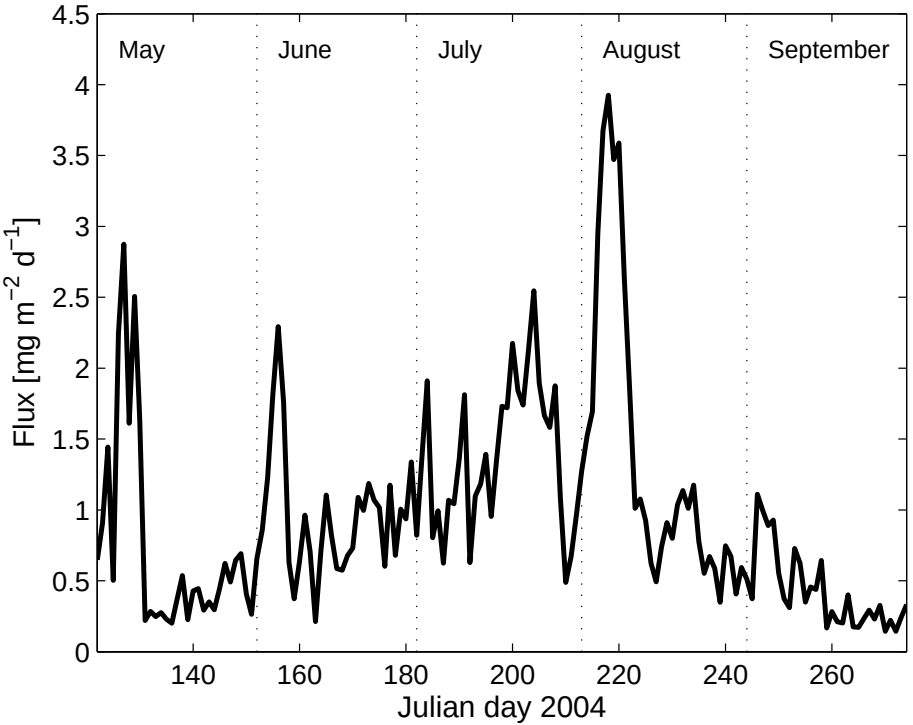

Fig. 5. Calculated daily isoprene emission for May–September 2004. According to the model, the total emission during the period was 150 mg m^{-2}.

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